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**WATER QUALITY AND PROTECTION:  
ENVIRONMENTAL ASPECTS**

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## **Chemical Element Composition and Amphipod Concentration Function in Baikal Littoral Zone**

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**Abstract**—Mass-spectrometry with inductively coupled plasma was used to determine the element composition of 19 amphipod species, most of which are widespread in the stony littoral of Lake Baikal. Amphipod composition was found to be dominated by  $Ca > P \geq S > K \geq Na > Cl > Mg > Sr \geq Br \geq Si$ . The concentrations of all elements determined in amphipods is greater than the respective concentrations in water. The amphipods were found to concentrate  $P > Br > Cu > Zn > Cd$  to the greatest extent relative to the element composition of water and  $Br > P \geq I > Ca > S > Cl \geq As > Sr$  relative to that of the stone substrate. The concentrations of Cr, Mn, Fe, Co, Cu, Zn, As, Mo, Cd, Pb, and Hg in 2003–2006 in the amphipods of the stony littoral of Baikal was not greater than their concentrations in the amphipods from conventionally non-polluted or weakly polluted aquatic ecosystems. The obtained results can be used as background values in environmental monitoring.

**Keywords:** Lake Baikal, littoral zone, amphipods, element chemical composition, concentration function

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### INTRODUCTION

The formation of the element composition of living organisms and their concentration function are closely related with the concentration of chemical elements in their habitat [23, 48]. By absorbing and accumulating vital macro- and microelements, Baikal aquatic organisms contribute to the formation of water element composition in the littoral (shallow zone), which extends from water edge to 20 m [3, 11–13]. Stony littoral is the richest zone in terms of the number of plant and animal species, their density and biomass [4, 8, 12, 13]. A dominating benthic group in this zone is amphipods, whose density can reach 6–8 thous. org./m<sup>2</sup> [10, 13, 15].

The benthic invertebrates consume chemical elements mostly with food, often accompanied by fine components of bottom sediments (BS) and water, containing dissolved and suspended forms of element compounds [41]. Most Baikal amphipods eat any organic material of plant or animal origin, commonly, with admixtures of mineral particles, detritus, and sponge spicules debris [21, 43]. In the chemical composition of crustaceans, a small portion is macro- and microelements of inert particles, absorbed by external-skeleton surface [49]. The tissues of aquatic invertebrates, along with biophilic, always contain elements Cd, Hg, Ag, Pb, which are toxic for organisms, even when in low concentrations [23]. Some metals (Fe,

Mn, Cu, Ag, Zn, Cd, Hg, Pb) accumulate in the exoskeleton and are disposed with exuvia [38, 42].

The basic component of the nutrient budget of many Baikal fish species [33, 34], amphipods are a source of vital macro- and microelements for them. Dead amphipods and their exuvia, containing a wide range of chemical elements are always present in the coastal detritus accumulations [31].

Benthic invertebrates can be an objective biogeochemical indicator of bottom water and BS pollution [35], and the chemical element composition of benthic organisms reflects the bioavailability of microelements in the habitats [42]. Currently, under the increasing anthropogenic pollution of Baikal coastal zone [57], data on amphipod element composition, representing natural biogeochemical background, are of particular importance. In the recent 5–6 years, many coastal areas of the lake show anomalously high development of filamentous alga of *Spirogyra* genus, mass disease and death of endemic Baikal sponges (from 30 to 100%), fouling of damaged sponges by cyanobacteria of *Phormidium* genus [57]. The data on the element composition of Baikal amphipods, published before, can be used as background values; however, they are few and fragmentary and embrace a limited number of species [5, 6, 14, 20, 24, 28, 29, 55].

The objective of this study is to determine the accumulation level of chemical elements in Baikal endemic amphipods in different life forms, collected under



**Fig. 1.** Scheme of sampling transects. (1) Berezovyi Cape, (2) Bol'shie Koty Bay, (3) Birkhin Bay, (4) Ol'khonskie Vorota Strait, (5) Izhimei Cape, (6) Bol'shoi Ushkanii Isl.

background natural biogeochemical conditions, to identify the elements that are concentrated by littoral amphipods to the greatest extent, and to choose the species most promising for biomonitoring.

## MATERIALS AND METHODS

The material of the study was 19 amphipod species, collected in the littoral of the Southern and Middle Baikal, the water areas of the islands of Ol'khon and Bol'shoi Ushkanii (Fig. 1; Table 1). The BS in these areas are dominated by boulder-pebble and pebble-sand soils. Considerable bed-rock outcrops can be seen [11].

Adult amphipods were collected from Baikal sponges and rock debris, taken by divers from depths of 1.5 to 12 m on six transects (Fig. 1) in 2003, 2004, and 2006. Once amphipods are determined, they were placed in aquariums with Baikal water, filtered through polypropylene element filters with pore diameter of 0.45  $\mu\text{m}$  and exposed in a refrigerator for two days. By the end of this time, their digestive tract had got free of the undigested food remains. The samples were taken to consist of several specimens of large species and dozens of specimens of middle and small-size species; the remaining soiling was removed under MBS-10 binocular, and the samples were washed by

distilled water. The crustaceans that died on the second day were isolated in separate samples. In addition, live *Brandtia latissima* with not empty intestines were also used to form samples. A big species *Pallasea cancellus* was used to analyze the element composition of the exoskeleton (cuticle) and inner tissue. The amphipods were cut along the central back line under a binocular and their soft tissues were extracted. All amphipod samples were dried in a desiccator at 30°C until air-dry, packed into polyethylene bags and placed in an exsiccator. Overall, 80 samples with 879 amphipods were taken. Before the analysis, the samples were pulverized in an agate mortar and dried until constant weight at 105°C. The preparation to the analysis was made by acid mineralization (70%  $\text{HNO}_3$ , 30%  $\text{H}_2\text{O}_2$ ) [26]. The nitric-acid decomposition of large-size amphipod samples, kept without food, left undissolved residue (up to 5% of sample mass). The residue after the decomposition of small species never exceeded 1%. The obtained residue was dissolved in 50% HF solution [26]. The component composition of the residue was determined under Carl Zeiss Jena light microscope with a magnification of  $\times 50$ –640. The surface of amphipod exoskeleton was examined by scanning electron microscope (Tesla BS-300).

The rock samples, after the collection of amphipods and the removal of fouling, were cleared to remove the weathered surface with following morphological and petrographic description. To determine the element composition, averaged samples of single-type rocks were crushed to particles 1–3 mm in size on a jaw crusher Pulverisette 1 (FRITSCH, Germany); quartering was used to take 5-g samples, which were pulverized in an agate mortar. The samples were prepared to the analysis by alkaline fusion of rocks with  $\text{Li}_2\text{BO}_3$  and leaching by 5%  $\text{HNO}_3$ .

Water samples were taken by divers into plastic syringes at the same transects (Fig. 1). Water was filtered through acetate-cellulose filters with pore diameter of 0.2  $\mu\text{m}$  into polypropylene test tubes and preserved by  $\text{HNO}_3$  extra-pure grade.

The element composition of the samples was determined by ICP-MS method. The analysis was carried out on mass-spectrometer Agilent 7500ce (Agilent Technologies) in Ultramikroanaliz Center at the Limnological Institute, Siberian Branch, Russian Academy of Sciences. The determinations of the element composition of the samples were verified using certified standard samples of muscle tissue of Baikal perch (Bok-2), garnet-biotite plagiogneiss (GBPg-1) (Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences), and abyssal Baikal water [54].

The concentration function of amphipods was evaluated with respect to water and BS by the formula:  $\text{BAC} = C_1/C_2$ . BAC is the biological accumulation coefficient, evaluated with respect to the element composition of water or a stone substrate; accordingly,

**Table 1.** Taxonomic position, occurrence, and ecological characteristic of the examined amphipods (dash means no data available) (taxonomy – [56]; live form characteristics – [30]; occurrence, habitat depth and body length – [1, 9, 30]; nutrition – [8, 21, 43]; straight swimmers means swim its dorsum upward)

| Taxa   | Habitat; soil  | Depth, m                       | Life form  | Body length, mm        | Food composition  |
|--|--|--------------------------------|--|------------------------|---|
| <i>Acanthogammarus victorii</i> (Dybowsky)<br><i>Brandtia latissima</i> (Dybowsky) | Southern Baikal up to Selenga shallows; sand, stones<br>Entire Baikal; stones with sponges and algae, rarer sand   | 3–90<br>1–65, commonly<br>2–40 | Epibenthic, walking, straight swimmers<br>Walking, lithophilous, with armed body | Up to 67<br>Up to 18.7 | Catches chironomids, crustaceans; eats dead fish<br>Benthic and planktonic diatoms, filamentous algae, macrophytes, oligochaetes, rotifers, crustaceans, detritus<br>Plant and animal organisms, living on sponges and settling from water column. Various algae are major food |
| <i>B. parasitica</i> (Dybowsky)  | Baikal, except for Selenga shallows; on sponges  | 1–60, rarely up to 200         | Obligate symbiont (epibiont) of Baikal sponges                                   | 10–11.5                |   |
| <i>Propachogammarus maximus</i> (Gajajew)  | Middle Baikal (western shore of Svyatoi Nos Peninsula), Northern Baikal (Ushkan'i Isls., Chivyrkuiskii Bay and further north to Sukhoi Cr.); stones, pebble, rare sand | 3–160                          | Nek, straight swimmer  | Up to 67               |   |
| <i>Carinogammarus wagai pallidus</i> (Dorogostaisky)                               | Southern Baikal, Selenga shallows; silt, stones, sand  | 14–400                         | –  | Up to 57               |   |
| <i>Eulimnogammarus cruentus</i> (Dorogostaisky)                                    | Baikal, except for Selenga shallows; stones, rarer sand, stones with sponges and algae   | 0.5–35, rarely up to 100       | Benthic, smooth-bodied swimmers form   | 20–23                  | Amphipods, entomostracans, oligochaetes, diatoms, detritus, fish  |
| <i>E. czerskii</i> (Dybowsky)  | Entire Baikal; stones, rarer sand; sponges, sometimes in hollows on sponge branches  | 1.5–25, rarer 40–125           | Benthic lithophilous, smooth-bodied swimmers form                                | 17–30                  | Detritus, filamentous and diatom algae, rotifers, oligochaetes; crustaceans dominate  |
| <i>E. grandimanus</i> Bazikalova   | Baikal, except for Barguzinskii, Chivyrkuiskii Bay, Selenga shallows; stones, pebble with sand and detritus, sponges, macrophytes                                      | 0–15, rarely up to 102         | Benthic lithophilous, smooth-bodied swimmers form                                | 6–8                    | Detritus, filamentous and diatom algae, macrophytes, rotifers, entomostracans, amphipods, may be fish   |
| <i>E. lividus</i> (Dybowsky)   | Baikal, except for Selenga shallows; stones  | 0–10, rarely up to 100         | Benthic lithophilous, smooth-bodied swimmers form                                | Up to 20–30            | Detritus, diatom, oligochaetes, fish, also eats young amphipods   |
| <i>E. maackii</i> (Gerstfeldt)   | Entire Baikal; stones, pebbles with sand and detritus, drowned wood, algae   | 0–15, rarely up to 40          | Benthic lithophilous, smooth-bodied swimmers form                                | Up to 27               | Diatoms, oligochaetes, crustaceans (many amphipods), fish   |

Table 1. (Contd.)

| Taxa   | Habitat; soil  | Depth, m                                   | Life form   | Body length, mm | Food composition   |
|--|--|--|---|-----------------|--|
| <i>E. verrucosus</i> (Gerstfeldt)            | Baikal, except for Selenga shallows; stones, pebble with sand and detritus, drowned wood, algae                                  | 0–12, most often at the shore under stones | Benthic lithophilous, smooth-bodied swimmers form | Up to 36        | Filamentous algae Ulotrix, benthic diatoms occur, crustaceans, detritus particles  |
| <i>E. capreolus</i> (Dybowsky)               | Southern Baikal, Middle Baikal (Ol'khonskie Vorota), Northern Baikal (Ushkan'i Isl.); sand, stones                               | 7–200, commonly below 25                   | Varying way of life                               | 12–21           | Rotifers, diatoms  |
| <i>E. fuscus</i> (Dybowsky)                  | Entire Baikal; sand, rarer silty sand, silt and stones   | 2–273, most often, up to 20                | –   | 25–35           | –  |
| <i>E. violaceus</i> (Dybowsky)               | Baikal, except for Selenga shallows; stones with sponges   | 1.5–140, commonly up to 10–30              | Symbiont biting holes in Baikal sponges           | 18–30           | In addition to sponge pieces, also recorded were individual benthic and planktonic diatoms, rotifers, and oligochaete's chaetae  |
| <i>E. marituji</i> Bazikalova                | Southern Baikal, Middle and Northern Baikal; sand, drowned wood, stones  | 0–30                                       | Benthic lithophilous, smooth-bodied swimmers form | 16–20           | Crustaceans, oligochaetes, some benthic diatoms, fungi hyphae  |
| <i>E. viridis</i> (Dybowsky)                 | Entire Baikal; stones  | 0–30, rarely up to 100                     | Benthic lithophilous, smooth-bodied swimmers form | 20–26           | Detritus, diatoms and filamentous algae, macrophytes, infusoria, rotifers, crustaceans, chironomids, terrestrial insects, fish   |
| <i>Heterogammarus sophianosii</i> (Dybowsky) | Entire Baikal; stones, rare silt and sand, algae   | 1–100                                      | –   | Up to 40        | –  |
| <i>Pallasea cancellus</i> (Pallas)           | Entire Baikal; stones and sand with vegetation, silt with sand and detritus  | 1–52, commonly 2–10                        | Phytophilous                                      | Up to 63–65     | Detritus, benthic and planktonic diatoms, filamentous and chrysophytean algae, rotifers, oligochaetes, crustaceans. In winter, under food deficiency, occurs in nets with fish |
| <i>P. kesslerii</i> (Dybowsky)               | Entire Baikal, most often in the Maloe More and Ol'khonskie Vorota Strait; sand, silt with crust, stones, sandy soil with plants | 1–100                                      | Phytophilous                                      | Up to 33        | Tubificidae  |

**Table 2.** Mean concentration ( $\pm$  standard deviation) of macroelements in water,  $\mu\text{g/L}$ , stone substrate and amphipods,  $\mu\text{g/g}$  dry mass (the concentrations of elements in water, stone substrate, and amphipods are rounded; in Tables 2, 3,  $n$  is the number of samples)

| Sample names                          | Na               | Mg             | P              | S              | Cl             | K                | Ca               |
|---------------------------------------|------------------|----------------|----------------|----------------|----------------|------------------|------------------|
| Water ( $n = 12$ )                    | 2600 $\pm$ 200   | 2400 $\pm$ 100 | 60 $\pm$ 10    | 470 $\pm$ 50   | 240 $\pm$ 30   | 750 $\pm$ 40     | 12600 $\pm$ 500  |
| Stone substrate*<br>( $n = 12$ )      | 28300 $\pm$ 1600 | 1100 $\pm$ 60  | 50 $\pm$ 10    | 600 $\pm$ 90   | 200 $\pm$ 60   | 29000 $\pm$ 2600 | 5100 $\pm$ 1600  |
| <i>A. victorii</i> ( $n = 3$ )        | 2300 $\pm$ 350   | 350 $\pm$ 50   | 2000 $\pm$ 140 | 2200 $\pm$ 330 | 870 $\pm$ 80   | 1330 $\pm$ 200   | 36000 $\pm$ 5400 |
| <i>B. latissima</i> ( $n = 9$ )       | 1800 $\pm$ 700   | 750 $\pm$ 200  | 2400 $\pm$ 600 | 3100 $\pm$ 600 | 970 $\pm$ 240  | 1430 $\pm$ 370   | 57300 $\pm$ 6000 |
| <i>B. parasitica</i> ( $n = 4$ )      | 1350 $\pm$ 340   | 500 $\pm$ 80   | 2600 $\pm$ 380 | 2400 $\pm$ 70  | 330 $\pm$ 70   | 1400 $\pm$ 220   | 45800 $\pm$ 8400 |
| <i>P. maximus</i> ( $n = 3$ )         | 3500 $\pm$ 530   | 850 $\pm$ 130  | 2700 $\pm$ 400 | 3300 $\pm$ 170 | 1400 $\pm$ 210 | 1900 $\pm$ 100   | 76000 $\pm$ 6800 |
| <i>C. waggii pallidus</i> ( $n = 3$ ) | 1330 $\pm$ 90    | 460 $\pm$ 40   | 2000 $\pm$ 280 | 2300 $\pm$ 160 | 520 $\pm$ 30   | 1220 $\pm$ 100   | 35000 $\pm$ 5200 |
| <i>E. cruentus</i> ( $n = 7$ )        | 1800 $\pm$ 800   | 550 $\pm$ 80   | 2500 $\pm$ 270 | 3000 $\pm$ 400 | 840 $\pm$ 230  | 1500 $\pm$ 300   | 39800 $\pm$ 3200 |
| <i>E. czerskii</i> ( $n = 5$ )        | 1600 $\pm$ 300   | 680 $\pm$ 30   | 3300 $\pm$ 250 | 3400 $\pm$ 300 | 600 $\pm$ 70   | 1500 $\pm$ 400   | 63600 $\pm$ 6600 |
| <i>E. grandimanus</i> ( $n = 3$ )     | 1400 $\pm$ 140   | 650 $\pm$ 70   | 3000 $\pm$ 300 | 3100 $\pm$ 270 | 400 $\pm$ 30   | 1600 $\pm$ 140   | 48000 $\pm$ 4600 |
| <i>E. lividus</i> ( $n = 3$ )         | 2000 $\pm$ 60    | 560 $\pm$ 60   | 2400 $\pm$ 400 | 3100 $\pm$ 250 | 660 $\pm$ 30   | 1600 $\pm$ 150   | 37000 $\pm$ 5000 |
| <i>E. maackii</i> ( $n = 3$ )         | 1750 $\pm$ 200   | 550 $\pm$ 80   | 2000 $\pm$ 150 | 3300 $\pm$ 60  | 430 $\pm$ 30   | 1300 $\pm$ 100   | 35000 $\pm$ 4600 |
| <i>E. verrucosus</i> ( $n = 5$ )      | 2200 $\pm$ 330   | 700 $\pm$ 170  | 2800 $\pm$ 200 | 3500 $\pm$ 180 | 720 $\pm$ 150  | 1800 $\pm$ 120   | 40000 $\pm$ 7000 |
| <i>E. capreolus</i> ( $n = 3$ )       | 2100 $\pm$ 150   | 600 $\pm$ 30   | 3200 $\pm$ 150 | 3150 $\pm$ 150 | 770 $\pm$ 50   | 2000 $\pm$ 120   | 39000 $\pm$ 2300 |
| <i>E. fuscus</i> ( $n = 3$ )          | 3200 $\pm$ 300   | 610 $\pm$ 65   | 3100 $\pm$ 300 | 3300 $\pm$ 300 | 1100 $\pm$ 120 | 2000 $\pm$ 170   | 51000 $\pm$ 6000 |
| <i>E. violaceus</i> ( $n = 4$ )       | 2200 $\pm$ 500   | 520 $\pm$ 60   | 2800 $\pm$ 350 | 3600 $\pm$ 480 | 620 $\pm$ 140  | 1800 $\pm$ 170   | 37000 $\pm$ 5700 |
| <i>E. marituji</i> ( $n = 4$ )        | 1500 $\pm$ 180   | 560 $\pm$ 80   | 2500 $\pm$ 350 | 3000 $\pm$ 350 | 450 $\pm$ 90   | 1600 $\pm$ 140   | 33500 $\pm$ 5000 |
| <i>E. viridis</i> ( $n = 8$ )         | 2100 $\pm$ 600   | 540 $\pm$ 140  | 2500 $\pm$ 470 | 3300 $\pm$ 510 | 750 $\pm$ 170  | 1800 $\pm$ 220   | 37100 $\pm$ 8600 |
| <i>H. sophianosii</i> ( $n = 3$ )     | 2500 $\pm$ 300   | 740 $\pm$ 120  | 3300 $\pm$ 500 | 3000 $\pm$ 300 | 800 $\pm$ 70   | 1900 $\pm$ 170   | 48000 $\pm$ 6000 |
| <i>P. cancellus</i> ( $n = 4$ )       | 1700 $\pm$ 200   | 470 $\pm$ 75   | 2000 $\pm$ 160 | 2600 $\pm$ 250 | 870 $\pm$ 30   | 1400 $\pm$ 20    | 40500 $\pm$ 2000 |
| <i>P. kesslerii</i> ( $n = 3$ )       | 1270 $\pm$ 40    | 680 $\pm$ 35   | 2200 $\pm$ 140 | 2500 $\pm$ 70  | 360 $\pm$ 30   | 1330 $\pm$ 70    | 46500 $\pm$ 700  |

\* Stone substrate of granitoid composition.

$C_1$  is the mean concentration of the element in the wet or dry mass of amphipods;  $C_2$  is the mean concentration of the element in water or rocks of granitoid composition, which are widespread all over the Baikal coast both as small outcrops and vast deposits [2]. The concentrations of water and ash in amphipod bodies were determined by thermobalance method.

The obtained data were processed by STATISTICA-7 software package. The significance of the differences between the mean concentrations of chemical elements in the samples under study was evaluated by Mann-Whitney test ( $U$ ).

## RESULTS OF STUDIES

Chemical elements occur in water in Baikal shallow zone in very low concentrations. A potential source of macro- and microelements, required for aquatic organisms, is stone substrate (Table 2, 3), which suffers intense destruction under littoral conditions [55].

The organisms of the examined amphipod consist of water (80–90%) and dry mass (ash residue) (20–24%). In the element composition, in the order of

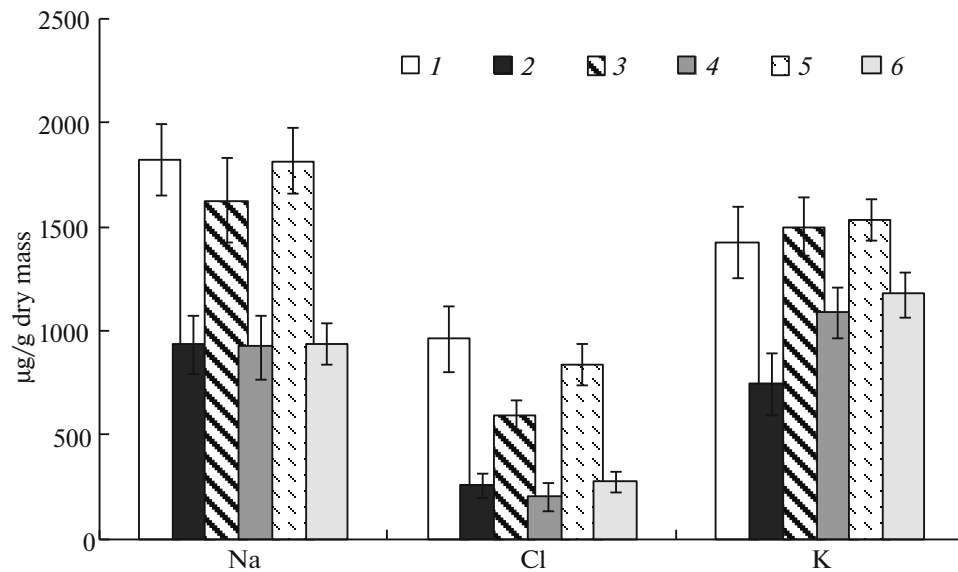
abundance, H, C, O, N are followed by Ca (several percent). The concentrations of S, P, Na, and K  $>$  1000, and Cl and Mg  $>$  300  $\mu\text{g/g}$  dry mass (Table 2). In the amphipods died on the second day, kept in aquariums without food, the amount of Na, K, and Cl is appreciably less (Fig. 2).

The largest differences were detected in the microelement composition of the amphipods. The concentrations of Sr, Br, Si in organisms of different species vary from 60 to 400  $\mu\text{g/g}$  dry mass. A wide variation range is typical of the concentrations of Al, Cu, Mn, and Fe. Ba, Zn, I, and Rb show similar concentrations. The concentrations of Ti, Cr, Co, Ni, As, Se, Mo vary within 0.1–3.0; and V, Cd, Pb, U, Th, within 0.02–0.10  $\mu\text{g/g}$  dry mass (Table 3). Low values are also typical of the concentrations of Li (0.06–0.19), B (0.01–0.36), Sc (0.03–0.12), Ga (0.007–0.033), Ge (0.002–0.010), Y (0.005–0.086), Zr (0.002–0.053), Ag (0.006–0.044), Sn (0.005–0.053), W (0.003–0.016), Tl ( $<$ 0.002–0.010), Hg (0.007–0.040  $\mu\text{g/g}$  dry mass).

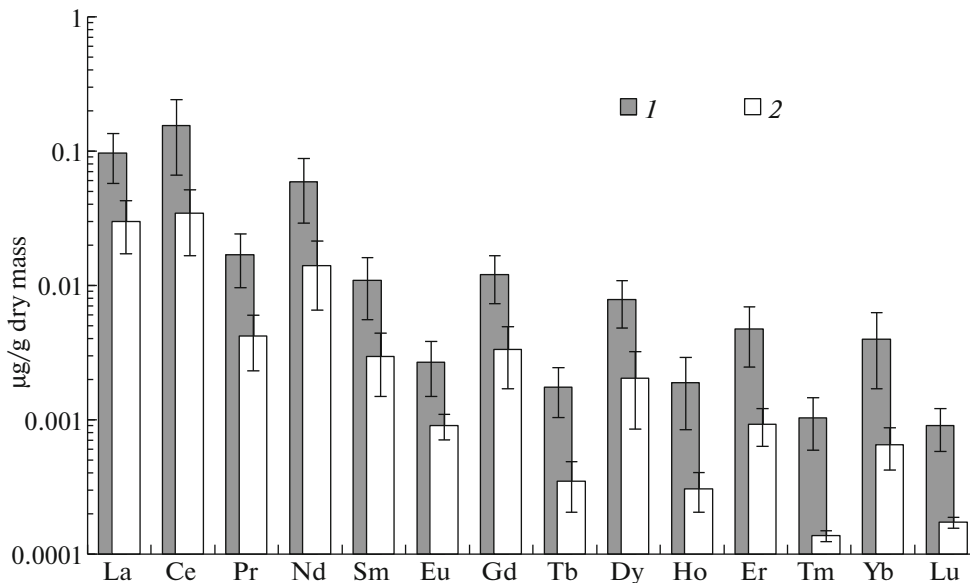
As typical of natural objects, the compositions of all examined amphipods showed higher concentrations of rare-earth elements (REE) with even atomic

**Table 3.** Mean concentration ( $\pm$  standard deviation) of microelements in water,  $\mu\text{g/L}$ , stone substrate and amphipods,  $\mu\text{g/g}$  dry mass (the elements, except for Pb, Th, and U, whose concentration in water is  $<0.1 \mu\text{g/g}$  dry mass, are not given in the table; the respective values are given in the text)

| Sample name                         | Al               | Si                | Ti              | V               | Cr               | Mn               | Fe               | Co              | Ni               | Cu                 | Zn                | As              |
|-------------------------------------|------------------|-------------------|-----------------|-----------------|------------------|------------------|------------------|-----------------|------------------|--------------------|-------------------|-----------------|
| Water ( $n = 12$ )                  | 4.4 $\pm$ 1.1    | 510 $\pm$ 110     | 0.15 $\pm$ 0.03 | 0.26 $\pm$ 0.04 | 0.18 $\pm$ 0.03  | 1.03 $\pm$ 0.43  | 90.3 $\pm$ 8.5   | 0.04 $\pm$ 0.01 | 0.74 $\pm$ 0.20  | 0.4 $\pm$ 0.1      | 0.80 $\pm$ 0.15   | 0.18 $\pm$ 0.02 |
| Stone substrate                     | 42700 $\pm$ 2500 | 120000 $\pm$ 5800 | 900 $\pm$ 50    | 4.22 $\pm$ 1.30 | 1.90 $\pm$ 0.60  | 170 $\pm$ 90     | 11000 $\pm$ 2400 | 2.07 $\pm$ 0.50 | 0.82 $\pm$ 0.23  | 11.2 $\pm$ 2.1     | 45.8 $\pm$ 5.9    | 0.25 $\pm$ 0.08 |
| <i>A. victorii</i> ( $n = 3$ )      | 3.3 $\pm$ 0.7    | 60 $\pm$ 20       | 0.19 $\pm$ 0.01 | 0.16 $\pm$ 0.02 | 0.46 $\pm$ 0.02  | 0.75 $\pm$ 0.04  | 14.2 $\pm$ 0.7   | 0.09 $\pm$ 0.01 | 0.06 $\pm$ 0.004 | 7.3 $\pm$ 1.1      | 24.0 $\pm$ 3.6    | 0.32 $\pm$ 0.05 |
| <i>B. latissima</i> ( $n = 9$ )     | 31.0 $\pm$ 3.9   | 270 $\pm$ 60      | 1.07 $\pm$ 0.31 | 0.23 $\pm$ 0.08 | 0.41 $\pm$ 0.17  | 19.5 $\pm$ 7.5   | 39.1 $\pm$ 7.6   | 0.25 $\pm$ 0.06 | 0.61 $\pm$ 0.20  | 11.0 $\pm$ 2.7     | 25.4 $\pm$ 8.7    | 1.18 $\pm$ 0.39 |
| <i>B. parsitica</i> ( $n = 4$ )     | 20.3 $\pm$ 5.7   | 150 $\pm$ 30      | 0.68 $\pm$ 0.23 | 0.16 $\pm$ 0.04 | 0.24 $\pm$ 0.05  | 4.75 $\pm$ 0.85  | 35.3 $\pm$ 4.1   | 0.15 $\pm$ 0.03 | 0.40 $\pm$ 0.04  | 17.0 $\pm$ 0.8     | 31.0 $\pm$ 7.3    | 0.82 $\pm$ 0.37 |
| <i>P. maximus</i> ( $n = 3$ )       | 110 $\pm$ 20     | 300 $\pm$ 60      | 3.20 $\pm$ 0.48 | 0.33 $\pm$ 0.04 | 0.41 $\pm$ 0.05  | 15.8 $\pm$ 2.2   | 100 $\pm$ 20     | 0.43 $\pm$ 0.04 | 2.30 $\pm$ 0.32  | 6.1 $\pm$ 0.4      | 28.0 $\pm$ 4.2    | 0.91 $\pm$ 0.14 |
| <i>C. wagi pallidus</i> ( $n = 3$ ) | 17.9 $\pm$ 3.0   | 180 $\pm$ 30      | 0.42 $\pm$ 0.06 | 0.09 $\pm$ 0.01 | 0.21 $\pm$ 0.03  | 5.80 $\pm$ 0.87  | 19.0 $\pm$ 1.5   | 0.11 $\pm$ 0.01 | 0.08 $\pm$ 0.01  | 3.6 $\pm$ 0.5      | 21.0 $\pm$ 1.3    | 0.34 $\pm$ 0.07 |
| <i>E. cruentus</i> ( $n = 7$ )      | 9.0 $\pm$ 3.4    | 140 $\pm$ 60      | 0.41 $\pm$ 0.11 | 0.11 $\pm$ 0.03 | 0.35 $\pm$ 0.04  | 4.28 $\pm$ 1.13  | 20.4 $\pm$ 3.4   | 0.17 $\pm$ 0.04 | 0.58 $\pm$ 0.20  | 13.7 $\pm$ 3.3     | 31.9 $\pm$ 4.8    | 0.83 $\pm$ 0.22 |
| <i>E. czerskii</i> ( $n = 5$ )      | 29.7 $\pm$ 7.6   | 220 $\pm$ 55      | 0.68 $\pm$ 0.20 | 0.19 $\pm$ 0.06 | 0.64 $\pm$ 0.26  | 8.48 $\pm$ 1.88  | 42.2 $\pm$ 17.8  | 0.25 $\pm$ 0.04 | 0.51 $\pm$ 0.12  | 13.1 $\pm$ 2.1     | 37.0 $\pm$ 4.4    | 1.03 $\pm$ 0.13 |
| <i>E. grandimanus</i> ( $n = 3$ )   | 80.0 $\pm$ 6.6   | 240 $\pm$ 80      | 3.30 $\pm$ 0.42 | 0.21 $\pm$ 0.02 | 0.37 $\pm$ 0.08  | 7.60 $\pm$ 2.36  | 74.5 $\pm$ 4.9   | 0.22 $\pm$ 0.06 | 0.59 $\pm$ 0.07  | 21.5 $\pm$ 3.5     | 40.3 $\pm$ 7.1    | 1.00 $\pm$ 0.17 |
| <i>E. lividus</i> ( $n = 3$ )       | 8.2 $\pm$ 0.8    | 140 $\pm$ 30      | 0.40 $\pm$ 0.09 | 0.10 $\pm$ 0.03 | 0.27 $\pm$ 0.02  | 7.30 $\pm$ 2.47  | 19.5 $\pm$ 0.7   | 0.13 $\pm$ 0.02 | 0.40 $\pm$ 0.04  | 14.0 $\pm$ 3.9     | 24.0 $\pm$ 4.6    | 0.89 $\pm$ 0.15 |
| <i>E. maaekii</i> ( $n = 3$ )       | 26.0 $\pm$ 1.2   | 130 $\pm$ 40      | 1.08 $\pm$ 0.39 | 0.08 $\pm$ 0.03 | 0.19 $\pm$ 0.06  | 6.00 $\pm$ 1.12  | 32.0 $\pm$ 11.3  | 0.30 $\pm$ 0.03 | 0.86 $\pm$ 0.21  | 8.8 $\pm$ 1.6      | 27.3 $\pm$ 2.3    | 0.96 $\pm$ 0.05 |
| <i>E. verrucosus</i> ( $n = 5$ )    | 36.3 $\pm$ 8.5   | 140 $\pm$ 20      | 1.35 $\pm$ 0.30 | 0.12 $\pm$ 0.02 | 0.36 $\pm$ 0.08  | 5.50 $\pm$ 1.68  | 31.6 $\pm$ 7.3   | 0.26 $\pm$ 0.07 | 0.59 $\pm$ 0.18  | 13.4 $\pm$ 2.2     | 37.6 $\pm$ 5.7    | 1.24 $\pm$ 0.14 |
| <i>E. capreolus</i> ( $n = 3$ )     | 20.0 $\pm$ 1.0   | 160 $\pm$ 20      | 0.72 $\pm$ 0.05 | 0.12 $\pm$ 0.01 | 0.33 $\pm$ 0.01  | 4.45 $\pm$ 0.25  | 35.5 $\pm$ 3.5   | 0.12 $\pm$ 0.01 | 0.38 $\pm$ 0.04  | 19.4 $\pm$ 0.3     | 25.0 $\pm$ 1.0    | 1.11 $\pm$ 0.06 |
| <i>E. fuscus</i> ( $n = 3$ )        | 7.0 $\pm$ 1.8    | 120 $\pm$ 20      | 0.67 $\pm$ 0.27 | 0.19 $\pm$ 0.01 | 0.46 $\pm$ 0.05  | 11.8 $\pm$ 1.2   | 34.0 $\pm$ 3.0   | 0.21 $\pm$ 0.02 | 0.59 $\pm$ 0.05  | 13.1 $\pm$ 1.1     | 32.5 $\pm$ 2.5    | 1.18 $\pm$ 0.11 |
| <i>E. violaceus</i> ( $n = 4$ )     | 4.4 $\pm$ 1.1    | 70 $\pm$ 20       | 0.30 $\pm$ 0.05 | 0.11 $\pm$ 0.02 | 0.19 $\pm$ 0.02  | 22.3 $\pm$ 6.5   | 34.0 $\pm$ 2.2   | 0.17 $\pm$ 0.06 | 0.19 $\pm$ 0.08  | 43.5 $\pm$ 11.6    | 32.8 $\pm$ 4.6    | 0.33 $\pm$ 0.07 |
| <i>E. maritujii</i> ( $n = 4$ )     | 6.7 $\pm$ 1.6    | 60 $\pm$ 10       | 0.38 $\pm$ 0.13 | 0.05 $\pm$ 0.01 | 0.22 $\pm$ 0.03  | 3.80 $\pm$ 0.71  | 18.9 $\pm$ 3.0   | 0.29 $\pm$ 0.05 | 0.67 $\pm$ 0.13  | 16.0 $\pm$ 2.4     | 33.5 $\pm$ 4.9    | 0.94 $\pm$ 0.13 |
| <i>E. viridis</i> ( $n = 8$ )       | 9.1 $\pm$ 1.8    | 80 $\pm$ 20       | 0.50 $\pm$ 0.13 | 0.09 $\pm$ 0.02 | 0.32 $\pm$ 0.10  | 4.34 $\pm$ 1.15  | 25.7 $\pm$ 5.0   | 0.17 $\pm$ 0.03 | 0.81 $\pm$ 0.20  | 15.3 $\pm$ 3.1     | 28.1 $\pm$ 3.3    | 1.04 $\pm$ 0.24 |
| <i>H. sophianosii</i> ( $n = 3$ )   | 5.1 $\pm$ 1.9    | 80 $\pm$ 10       | 0.30 $\pm$ 0.10 | 0.06 $\pm$ 0.01 | 0.18 $\pm$ 0.04  | 3.35 $\pm$ 0.65  | 29.0 $\pm$ 4.0   | 0.31 $\pm$ 0.05 | 0.16 $\pm$ 0.02  | 14.1 $\pm$ 1.6     | 32.0 $\pm$ 5.0    | 0.69 $\pm$ 0.12 |
| <i>P. cancellus</i> ( $n = 4$ )     | 15.1 $\pm$ 1.7   | 80 $\pm$ 25       | 0.39 $\pm$ 0.18 | 0.04 $\pm$ 0.01 | 0.18 $\pm$ 0.02  | 3.30 $\pm$ 0.70  | 27.0 $\pm$ 5.3   | 0.16 $\pm$ 0.03 | 0.36 $\pm$ 0.11  | 7.6 $\pm$ 3.0      | 27.8 $\pm$ 4.5    | 1.03 $\pm$ 0.17 |
| <i>P. kesslerii</i> ( $n = 3$ )     | 60.0 $\pm$ 9.9   | 210 $\pm$ 10      | 2.85 $\pm$ 0.07 | 0.15 $\pm$ 0.02 | 0.26 $\pm$ 0.01  | 5.1 $\pm$ 0.28   | 66.5 $\pm$ 10.6  | 0.19 $\pm$ 0.01 | 0.14 $\pm$ 0.01  | 12.1 $\pm$ 1.8     | 40.5 $\pm$ 2.9    | 0.82 $\pm$ 0.02 |
| Sample name                         | Se               | Br                | Rb              | Sr              | Mo               | Cd               | I                | Ba              | Pb               | Th                 | U                 |                 |
| Water ( $n = 12$ )                  | 0.08 $\pm$ 0.01  | 5.9 $\pm$ 0.4     | 0.43 $\pm$ 0.02 | 79.8 $\pm$ 4.1  | 0.73 $\pm$ 0.04  | 0.01 $\pm$ 0.002 | 1.26 $\pm$ 0.12  | 10.1 $\pm$ 1.7  | 0.09 $\pm$ 0.03  | 0.001 $\pm$ 0.0001 | 0.39 $\pm$ 0.02   |                 |
| Stone substrate ( $n = 12$ )        | 0.24 $\pm$ 0.05  | 0.48 $\pm$ 0.10   | 82.8 $\pm$ 9.5  | 150 $\pm$ 20    | 0.53 $\pm$ 0.05  | 0.08 $\pm$ 0.03  | 0.05 $\pm$ 0.03  | 960 $\pm$ 300   | 12.6 $\pm$ 4.2   | 12.2 $\pm$ 4.6     | 0.92 $\pm$ 0.30   |                 |
| <i>A. victorii</i> ( $n = 3$ )      | 0.20 $\pm$ 0.02  | 220 $\pm$ 20      | 2.3 $\pm$ 0.16  | 200 $\pm$ 20    | 0.14 $\pm$ 0.01  | 0.13 $\pm$ 0.01  | 1.56 $\pm$ 0.31  | 23.0 $\pm$ 4.6  | 0.02 $\pm$ 0.004 | 0.005 $\pm$ 0.001  | <0.002            |                 |
| <i>B. latissima</i> ( $n = 9$ )     | 0.30 $\pm$ 0.11  | 260 $\pm$ 60      | 2.45 $\pm$ 0.60 | 270 $\pm$ 90    | 0.19 $\pm$ 0.05  | 0.10 $\pm$ 0.04  | 3.97 $\pm$ 0.90  | 36.8 $\pm$ 11.1 | 0.09 $\pm$ 0.02  | 0.017 $\pm$ 0.007  | 0.13 $\pm$ 0.04   |                 |
| <i>B. parsitica</i> ( $n = 4$ )     | 0.43 $\pm$ 0.11  | 160 $\pm$ 20      | 2.87 $\pm$ 0.23 | 220 $\pm$ 40    | 0.13 $\pm$ 0.02  | 0.15 $\pm$ 0.04  | 3.15 $\pm$ 0.66  | 26.5 $\pm$ 4.2  | 0.14 $\pm$ 0.03  | 0.006 $\pm$ 0.002  | 0.12 $\pm$ 0.06   |                 |
| <i>P. maximus</i> ( $n = 3$ )       | 0.66 $\pm$ 0.06  | 200 $\pm$ 30      | 3.00 $\pm$ 0.24 | 360 $\pm$ 50    | 0.18 $\pm$ 0.01  | 0.35 $\pm$ 0.04  | 3.50 $\pm$ 0.32  | 41.0 $\pm$ 3.7  | 0.30 $\pm$ 0.02  | 0.014 $\pm$ 0.001  | 0.18 $\pm$ 0.01   |                 |
| <i>C. wagi pallidus</i> ( $n = 3$ ) | 0.18 $\pm$ 0.02  | 320 $\pm$ 20      | 1.85 $\pm$ 0.22 | 170 $\pm$ 25    | 0.15 $\pm$ 0.01  | 0.05 $\pm$ 0.007 | 1.76 $\pm$ 0.16  | 28.0 $\pm$ 4.2  | 0.07 $\pm$ 0.014 | 0.004 $\pm$ 0.001  | 0.018 $\pm$ 0.003 |                 |
| <i>E. cruentus</i> ( $n = 7$ )      | 0.35 $\pm$ 0.09  | 240 $\pm$ 30      | 2.78 $\pm$ 0.68 | 200 $\pm$ 20    | 0.16 $\pm$ 0.03  | 0.24 $\pm$ 0.08  | 2.69 $\pm$ 0.38  | 30.9 $\pm$ 4.8  | 0.11 $\pm$ 0.04  | 0.004 $\pm$ 0.001  | 0.049 $\pm$ 0.016 |                 |
| <i>E. czerskii</i> ( $n = 5$ )      | 0.39 $\pm$ 0.10  | 270 $\pm$ 70      | 2.80 $\pm$ 0.24 | 320 $\pm$ 20    | 0.16 $\pm$ 0.02  | 0.24 $\pm$ 0.08  | 3.30 $\pm$ 0.43  | 42.6 $\pm$ 5.7  | 0.06 $\pm$ 0.02  | 0.005 $\pm$ 0.002  | 0.062 $\pm$ 0.023 |                 |
| <i>E. grandimanus</i> ( $n = 3$ )   | 0.50 $\pm$ 0.07  | 280 $\pm$ 20      | 2.77 $\pm$ 0.25 | 230 $\pm$ 20    | 0.16 $\pm$ 0.03  | 0.11 $\pm$ 0.03  | 4.03 $\pm$ 0.42  | 41.0 $\pm$ 6.2  | 0.16 $\pm$ 0.02  | 0.022 $\pm$ 0.013  | 0.13 $\pm$ 0.02   |                 |
| <i>E. lividus</i> ( $n = 3$ )       | 0.27 $\pm$ 0.06  | 210 $\pm$ 20      | 2.67 $\pm$ 0.12 | 180 $\pm$ 40    | 0.14 $\pm$ 0.02  | 0.11 $\pm$ 0.03  | 2.50 $\pm$ 0.46  | 24.7 $\pm$ 3.8  | 0.03 $\pm$ 0.01  | 0.004 $\pm$ 0.001  | 0.040 $\pm$ 0.014 |                 |
| <i>E. maaekii</i> ( $n = 3$ )       | 0.30 $\pm$ 0.05  | 280 $\pm$ 60      | 2.05 $\pm$ 0.23 | 170 $\pm$ 20    | 0.12 $\pm$ 0.03  | 0.05 $\pm$ 0.01  | 2.15 $\pm$ 0.36  | 18.3 $\pm$ 2.4  | 0.10 $\pm$ 0.02  | 0.012 $\pm$ 0.002  | 0.029 $\pm$ 0.001 |                 |
| <i>E. verrucosus</i> ( $n = 5$ )    | 0.32 $\pm$ 0.04  | 250 $\pm$ 40      | 2.90 $\pm$ 0.14 | 200 $\pm$ 30    | 0.16 $\pm$ 0.04  | 0.06 $\pm$ 0.006 | 1.88 $\pm$ 0.22  | 29.0 $\pm$ 2.9  | 0.12 $\pm$ 0.05  | 0.010 $\pm$ 0.001  | 0.028 $\pm$ 0.004 |                 |
| <i>E. capreolus</i> ( $n = 3$ )     | 0.46 $\pm$ 0.01  | 190 $\pm$ 10      | 3.20 $\pm$ 0.10 | 190 $\pm$ 10    | 0.17 $\pm$ 0.01  | 0.04 $\pm$ 0.001 | 1.77 $\pm$ 0.04  | 32.0 $\pm$ 2.0  | 0.23 $\pm$ 0.02  | <0.001             | 0.043 $\pm$ 0.004 |                 |
| <i>E. fuscus</i> ( $n = 3$ )        | 0.49 $\pm$ 0.04  | 240 $\pm$ 20      | 3.35 $\pm$ 0.25 | 240 $\pm$ 30    | 0.19 $\pm$ 0.003 | 0.06 $\pm$ 0.005 | 2.55 $\pm$ 0.25  | 30.5 $\pm$ 3.5  | 0.06 $\pm$ 0.003 | <0.001             | 0.053 $\pm$ 0.004 |                 |
| <i>E. violaceus</i> ( $n = 4$ )     | 0.84 $\pm$ 0.17  | 230 $\pm$ 30      | 2.55 $\pm$ 0.13 | 180 $\pm$ 20    | 0.25 $\pm$ 0.05  | 0.57 $\pm$ 0.19  | 11.70 $\pm$ 2.40 | 20.8 $\pm$ 4.6  | 0.12 $\pm$ 0.04  | 0.005 $\pm$ 0.001  | 0.021 $\pm$ 0.010 |                 |
| <i>E. maritujii</i> ( $n = 4$ )     | 0.31 $\pm$ 0.06  | 180 $\pm$ 40      | 2.40 $\pm$ 0.14 | 170 $\pm$ 25    | 0.11 $\pm$ 0.02  | 0.05 $\pm$ 0.01  | 1.23 $\pm$ 0.15  | 21.5 $\pm$ 3.6  | 0.02 $\pm$ 0.006 | <0.001             | 0.020 $\pm$ 0.004 |                 |
| <i>E. viridis</i> ( $n = 8$ )       | 0.27 $\pm$ 0.03  | 210 $\pm$ 40      | 3.00 $\pm$ 0.52 | 190 $\pm$ 50    | 0.18 $\pm$ 0.04  | 0.06 $\pm$ 0.01  | 2.45 $\pm$ 0.47  | 24.4 $\pm$ 4.0  | 0.06 $\pm$ 0.01  | 0.003 $\pm$ 0.001  | 0.027 $\pm$ 0.005 |                 |
| <i>H. sophianosii</i> ( $n = 3$ )   | 0.54 $\pm$ 0.05  | 260 $\pm$ 20      | 2.95 $\pm$ 0.25 | 250 $\pm$ 30    | 0.14 $\pm$ 0.02  | 0.07 $\pm$ 0.01  | 2.30 $\pm$ 0.30  | 47.5 $\pm$ 5.5  | 0.05 $\pm$ 0.004 | <0.001             | 0.025 $\pm$ 0.005 |                 |
| <i>P. cancellus</i> ( $n = 4$ )     | 0.26 $\pm$ 0.05  | 190 $\pm$ 40      | 2.55 $\pm$ 0.50 | 230 $\pm$ 70    | 0.10 $\pm$ 0.02  | 0.03 $\pm$ 0.01  | 2.05 $\pm$ 0.40  | 24.1 $\pm$ 7.2  | 0.07 $\pm$ 0.03  | 0.004 $\pm$ 0.001  | 0.017 $\pm$ 0.006 |                 |
| <i>P. kesslerii</i> ( $n = 3$ )     | 0.50 $\pm$ 0.02  | 120 $\pm$ 10      | 2.35 $\pm$ 0.10 | 260 $\pm$ 10    | 0.11 $\pm$ 0.01  | 0.03 $\pm$ 0.002 | 1.84 $\pm$ 0.057 | 37.5 $\pm$ 1.0  | 0.19 $\pm$ 0.02  | 0.020 $\pm$ 0.004  | 0.016 $\pm$ 0.004 |                 |



**Fig. 2.** Mean concentration ( $\pm$  standard deviation) of Na, Cl, and K in three amphipod species ( $n = 3$ ): (1) *B. latissima* alive, (2) dead; (3) *E. czerskii* alive, (4) dead; (5) *E. cruentus* alive, (6) dead.  $U = 0$ ;  $U_{kr} = 2$ ,  $p < 0.05$  for all compared pairs. The samples were taken on March 26, 2003, at Berezovyi Cape at a depth of 10–12 m.

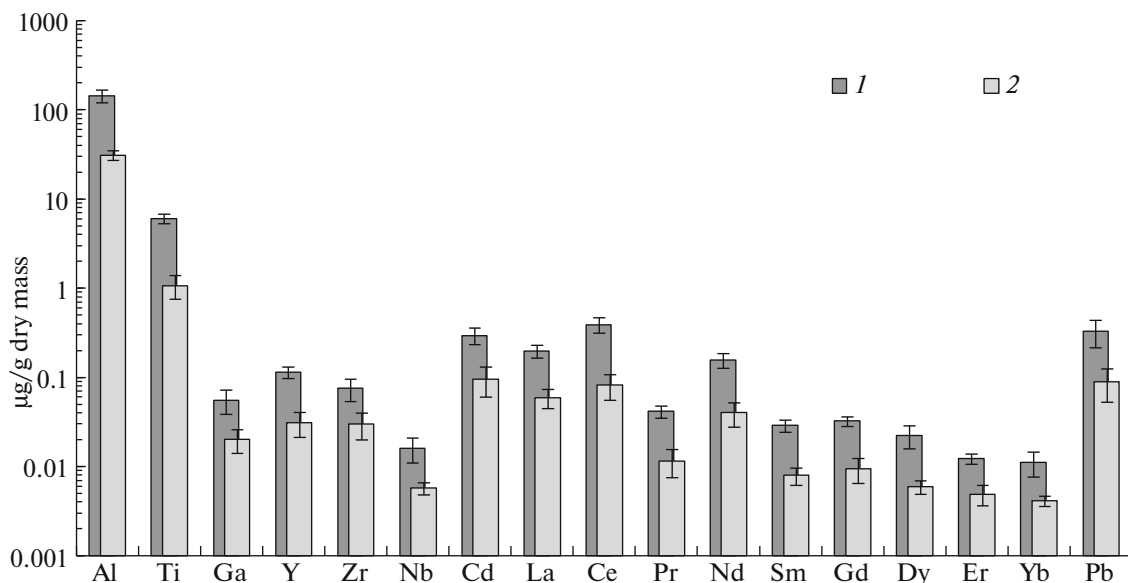


**Fig. 3.** General regularities of REE distribution and their mean concentration ( $\pm$  standard deviation) in amphipods: (1) *B. latissima*, *P. maximus*, *E. grandimanus*, *E. maackii*, *E. verrucosus*, *P. kesslerii*; (2) *B. parasitica*, *E. cruentus*, *E. czerskii*, *E. violaceus*, *E. marituji*, *E. viridis*, *A. victorii*, *C. waggii pallidus*, *E. lividus*, *E. fuscus*, *E. capreolus*, *H. sophianosii*, *P. cancellus*.

numbers (Ce, Nd, Sm, Gd, Dy, Er, Yb), as compared with elements with odd numbers (Pr, Eu, Tb, Ho, Tm, Lu), and enrichment by light REE (La, Ce, Pr, Nd) relative to higher ones (Tb, Dy, Ho, Er, Tm, Yb, Lu), the concentration of which lies in the range of very low values (Fig. 3). At the similar distribution of these elements in amphipod composition, some species have relatively high (*B. latissima*, *P. maximus*, *E. grandimanus*, *E. maackii*, *E. verrucosus*, *P. kesslerii*) and rel-

atively low (*B. parasitica*, *E. cruentus*, *E. czerskii*, *E. violaceus*, *E. marituji*, *E. viridis*, *A. victorii*, *C. waggii pallidus*, *E. lividus*, *E. fuscus*, *E. capreolus*, *H. sophianosii*, *P. cancellus*) REE concentrations ( $p < 0.001$ ) (Fig. 3).

The lowest concentrations in amphipods are those of Be ( $<0.003$ ), Nb ( $<0.0008$ – $0.0078$ ), Pd ( $<0.0001$ – $0.0009$ ), Sb ( $<0.006$ – $0.008$ ), Cs ( $<0.002$ ), Eu ( $0.0004$ – $0.0043$ ), Tb ( $0.0001$ – $0.0033$ ), Tm



**Fig. 4.** Mean concentration ( $\pm$  standard deviation) of chemical elements in *B. latissima* ( $n = 4$ ): (1) with digestive tract not emptied; (2) with emptied digestive tract.  $U = 0$ ,  $U_{kr} = 1$ ,  $p < 0.05$  for all elements. The samples were taken on March 13, 2006 at Berezoyvi Cape at a depth of 8.5 m.

(<0.0002–0.0013), Lu (<0.0001–0.0023), Au (<0.0008), Hf (<0.0003–0.0008), Ta (0.0003–0.0050), Bi (<0.0003–0.0040 µg/g dry mass). Higher concentration of Al, Ti, Ga, Y, Zr, Nb, Cd, P3Θ, Pb was found in the composition of *B. latissima* with not emptied intestines (Fig. 4).

The analysis of the composition of the exoskeleton and the body with removed cuticle covers of a common phytophilous species *P. cancellus* showed that the exoskeleton, in addition to Ca, contains much P, S, Mg, Na, Br, Si, Sr, and appreciable amounts of Cl, Ba, Fe, Al, Zn, Mn, I, and Cu (Fig. 5). The concentrations of Ti, As, Rb, Ni, Mo, Cr, B, V, Co, Se, and Sc are <1; and those of other analyzed elements are <0.1 µg/g dry mass. Compared with the body, the element composition of exoskeleton contains 4–7 times more Ca, Sr, Ba, Si, and Br, 1.5–2 times more Na, I, Mg, Al, and less P, S, Cl, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb; similar concentrations were recorded for K, Co, Rb, and Mo (Fig. 5). The overall chemical element composition of exoskeleton also contains elements accumulated by diatom algae, which colonize amphipod surfaces, as well as elements of fine solid particles, absorbed by exoskeleton surface (Fig. 6). Thus, the proportion of precipitate after the decomposition by nitric acid of samples consisting of *Propachygammarus maximus* specimens, kept without food for two days, was 3–5%; they were represented by diatom valves and an admixture of mineral particles <0.001 mm in size. The element composition of the precipitate included 2–3% Si, large amounts of Al (1000–1100), Fe (600–700), Ti (120–70), Zr (2.5–3.0), and V (1.70–2.90 µg/g dry mass).

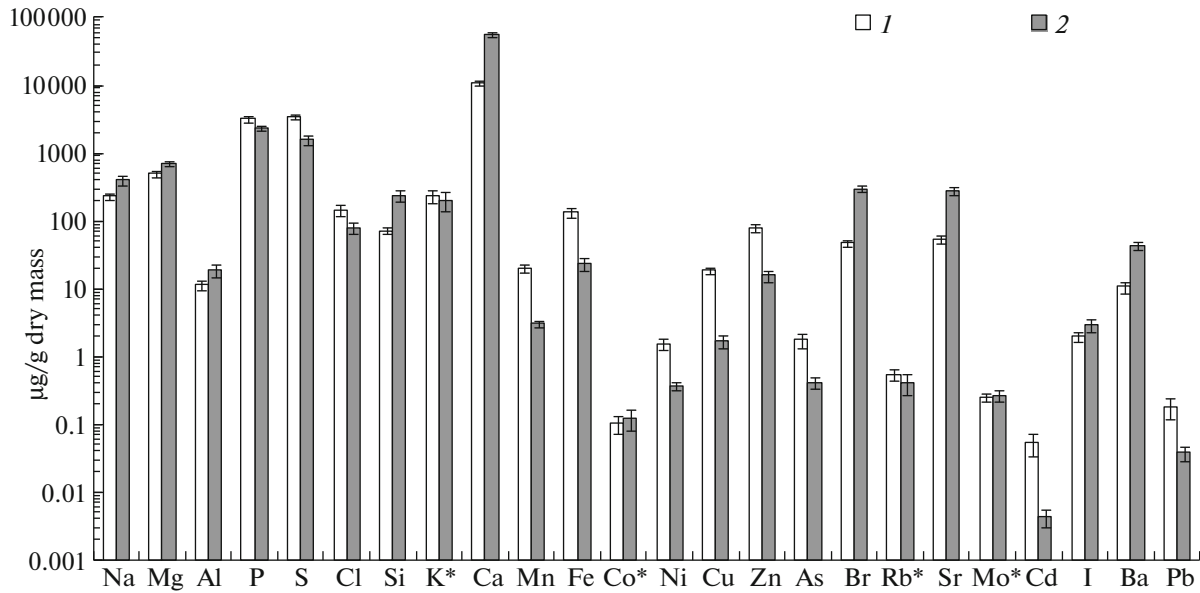
The formation of the element composition of hydrosphere takes place in the system: water  $\rightleftharpoons$  rocks  $\rightleftharpoons$  living matter [23]; therefore, the ability of amphipods to concentrate chemical elements was characterized by the ratio of their concentration in crustaceans to the mean concentration in water and rock substrate. This ratio characterizes the degree of element concentration in the living organism relative to the habitat [5]. The concentration of all analyzed elements in the amphipods of Baikal littoral is much greater than their concentrations in water. The degree of concentration by the examined amphipods relative to water is largest for P, Br, and Cu and similar in chemical properties Zn and Cd; and that relative to stone substrate is largest for  $Br > P \geq I > Ca > S > Cl \geq As > Sr$  (Table 4, 5).

## DISCUSSION OF RESULTS

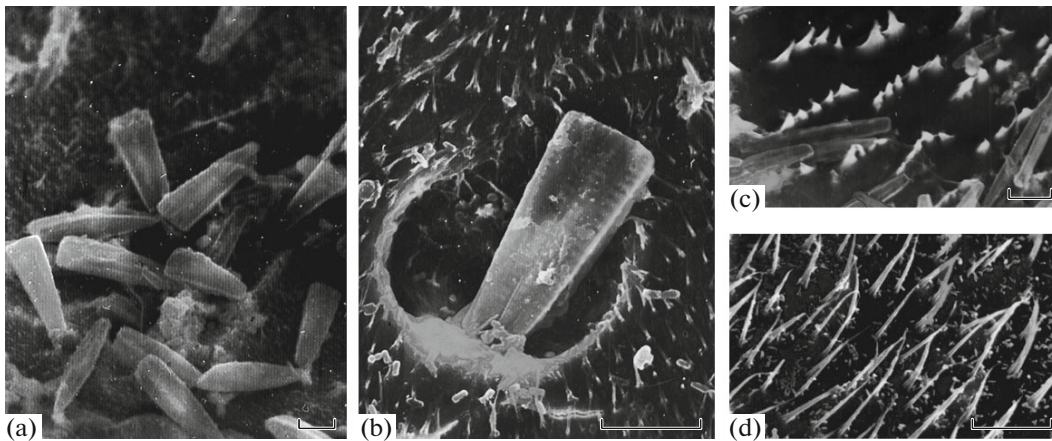
A characteristic feature of crustaceans is their exoskeleton, i.e., a layered chitin–protein complex. The two inner layers are impregnated by calcium carbonate. During moulting, some calcium is removed with exuvia, and some is accumulated in the pre-moulting period in caecum intestinal [46, 50]. The surface of amphipod cuticles has microscopic projections (microtriches) [22], which increase the specific surface of the exoskeleton and, accordingly, its sorption capacity.

All amphipod species, examined by the authors, show high Ca content, which is 3–5 times the total concentration of other elements (Table 2). The largest amount of Ca was recorded in *P. maximus*, *B. latissima*, *Eulimnogammarus czerskii*; the former two,





**Fig. 5.** Mean concentration ( $\pm$  standard deviation) of macro- and microelements: (1) in internal tissues, (2) in the exoskeleton of *P. cancellus* ( $n = 3$ ).  $U = 0.5$ ,  $U_{kr} = 2$ ,  $p < 0.05$ . The symbol \* marks insignificant differences. The samples were taken on July 5, 2004 at Berezovyi Cape at a depth of 3 m.



**Fig. 6.** Diatom algae, bacteria, and fine solid particles on the surface of an amphipod cuticle: (a, b) detritus particles and colonies of benthic diatoms *Gomphonema* on *B. parasitica*, (c) colonies of benthic diatom fouling on *P. maximus*, (d) *H. sophianosii* with microorganisms and detritus particles. Scale of 10  $\mu\text{m}$ .

despite of the difference in size, have very thick cuticular covers with a complex microsculpture, which increases exoskeleton strength. The variations in the concentration of Ca and many other elements can be due to the physiological state and the morphological features of the species, as well as their habitat conditions, dietary habits, mineral composition, and the amount of suspension adsorbed on exoskeleton surface. Among the examined large-size species with thick exoskeleton, the highest Ca concentration ( $p < 0.05$ ) was found in *P. maximus*. Unlike other giant species—*Acanthogammarus victorii* and *Carinogammarus waggioi*—this one lives in Baikal zones

(Table 1) with a wide occurrence of carbonate rocks, the dissolution of which enriches the bottom layer with alkaline-earth elements [27].

The ratio Ca/Mg in the examined species is 60–100. The flexibility and rigidity of the cuticular covers of crustaceans are determined by the optimal proportions of these elements [46]. According to averaged data, the ratio of Ca and Sr, closely correlated in the biosphere, in living matter, is 250 [7], and that in the examined amphipods and water in Baikal shallow zone is 160–200.

The concentration of Br, which also concentrates mostly in exoskeletons (Fig. 5), varies from 120 to

**Table 4.** BAC of microelements with high accumulation degree (>1000) and macroelements in amphipod wet mass relative to water element composition

| Species                   | Na  | Mg | P    | S    | Cl  | K   | Ca   | Cu    | Zn   | Br   | Cd    |
|---------------------------|-----|----|------|------|-----|-----|------|-------|------|------|-------|
| <i>A. victorii</i>        | 150 | 30 | 5800 | 800  | 610 | 300 | 490  | 3400  | 5100 | 6300 | 3700  |
| <i>B. latissima</i>       | 119 | 50 | 7000 | 1100 | 680 | 330 | 780  | 5200  | 5400 | 7600 | 2700  |
| <i>B. parasitica</i>      | 90  | 40 | 7500 | 870  | 230 | 330 | 620  | 8000  | 6600 | 4600 | 4100  |
| <i>P. maximus</i>         | 230 | 60 | 7800 | 1200 | 960 | 430 | 1030 | 2900  | 5900 | 5800 | 9900  |
| <i>C. waggii pallidus</i> | 90  | 30 | 5800 | 800  | 360 | 280 | 470  | 1700  | 5800 | 9200 | 1400  |
| <i>E. cruentus</i>        | 120 | 40 | 7200 | 1100 | 590 | 350 | 540  | 6500  | 6800 | 6900 | 6800  |
| <i>E. czerskii</i>        | 110 | 50 | 9700 | 1200 | 420 | 340 | 860  | 6200  | 7900 | 7800 | 6800  |
| <i>E. grandimanus</i>     | 90  | 50 | 8800 | 1100 | 280 | 370 | 650  | 10100 | 8600 | 8100 | 3000  |
| <i>E. lividus</i>         | 130 | 40 | 7000 | 1100 | 460 | 380 | 500  | 6600  | 5100 | 6100 | 3100  |
| <i>E. maackii</i>         | 110 | 40 | 5700 | 1200 | 300 | 290 | 470  | 4100  | 7100 | 8100 | 1500  |
| <i>E. verrucosus</i>      | 150 | 50 | 8100 | 1280 | 500 | 410 | 540  | 6300  | 8000 | 7200 | 1600  |
| <i>E. capreolus</i>       | 130 | 40 | 9300 | 1100 | 540 | 450 | 530  | 9100  | 5300 | 5400 | 1100  |
| <i>E. fuscus</i>          | 210 | 40 | 9000 | 1200 | 780 | 460 | 690  | 6200  | 6900 | 6700 | 1600  |
| <i>E. violaceus</i>       | 150 | 40 | 8000 | 1300 | 430 | 420 | 510  | 20500 | 7000 | 6700 | 16000 |
| <i>E. marituji</i>        | 100 | 40 | 7200 | 1100 | 320 | 370 | 450  | 7500  | 4500 | 5200 | 1500  |
| <i>E. viridis</i>         | 140 | 40 | 7400 | 1200 | 530 | 420 | 500  | 7200  | 6000 | 5900 | 1800  |
| <i>H. sophianosii</i>     | 160 | 50 | 9600 | 1100 | 550 | 440 | 650  | 6600  | 6800 | 7300 | 1900  |
| <i>P. cancellus</i>       | 110 | 30 | 5900 | 950  | 610 | 330 | 550  | 3600  | 5900 | 5500 | 770   |
| <i>P. kesslerii</i>       | 80  | 50 | 6400 | 900  | 250 | 300 | 630  | 5700  | 8590 | 3500 | 710   |

320 µg/g dry mass. High concentrations of Br were found in many marine invertebrates in their dactyli, claws, and other “instruments,” subject to considerable mechanical loads [37, 52]. In addition to Ca, an important role in the strengthening of the cutting part of mandible in deep-water species *Acanthogammarus grewingkii* belongs to Br and Si [44]. The main advantage of brominated over calcareous cuticle is its resistance to cracking [53]. The ability to accumulate enough Br (Table 3) is of great importance for Baikal amphipods, living in low-mineralization water.

The concentration of Si in the organisms of most of the examined species is >120 µg/g dry mass (Table 3). The amount of Si in amphipods can reflect not only its concentration in animal tissues, but also the density of diatoms living on them and the suspension precipitated onto exoskeleton surface (Fig. 6).

All amphipods accumulate nearly equal amounts of vital elements, such as S and P. *P. maximus*, *A. victorii*, and *Eulimnogammarus fuscus* show higher concentrations of Na and K (Na/K of 1.6 to 1.8;  $p < 0.05$ ). Such relationship is clearly due to the predominance of animal food, which generally contains more Na than vegetable food does. Thus, *A. victorii* is known to prey and to eat dead fish [8]. In the composition of the organisms of other examined species, showing flexible feeding behavior (Table 1), Na/K ~1.

In amphipod microelement composition, the range of concentration variations was widest for Al, Ti,

Mn, Fe, Ni, Cu, Cd (Table 3). The highest concentrations of Cu, I, Cd ( $p < 0.001$ ) were recorded in a symbiont of Baikal sponges *Eulimnogammarus violaceus*. Only this species shows similar concentrations of Cu and Zn, while other amphipods, as well as many marine crustaceans [6, 36], accumulate more Zn ( $p < 0.001$ ). The ratio Zn/Cu in the examined amphipods is 1.3–4.6.

The concentration of Zn and Cd in Baikal amphipods follows the general regularity in the distribution of these elements in the Earth crust, whose Zn content is ~400 times greater than that of Cd [7]. In the stony substrate of Baikal littoral, Zn/Cd is ~570, and that in water is 130. In *Eulimnogammarus cruentus*, *E. violaceus*, *E. czerskii*, *E. lividus*, *P. maximus*, *A. victorii*, *Brandtia parasitica*, *B. latissima*, the ratio Zn/Cd is 60–250, while in other species, it is 400–1600. The same ratio on amphipods from relatively nonpolluted and weakly polluted aquatic ecosystems of European Russian and the mountain streams in the Caucasus and Tien-Shan, this ratio varies within 90–200 [23].

*E. violaceus* shows the minimal value of the ratio Fe/Mn – 1.5 ( $p < 0.05$ ). In *E. lividus*, *E. fuscus*, *B. latissima*, *C. waggii pallidus*, the ratio Fe/Mn is 2–3 ( $p < 0.05$ ), while in other species, it is 5–20 ( $p < 0.01$ ) (Table 3). In the averaged composition of living matter and marine crustaceans, Fe/Mn ~ 10 [7, 36]. The concentration of Fe is highest ( $p < 0.01$ ) in *P. maximus*, *Eulimnogammarus grandimanus*, and *Pallasea kesslerii*.

**Table 5.** BAC  $\geq 1$  of macro- and microelements in amphipod dry mass relative to the element composition of stone substrate

| Species                   | P    | S    | Cl   | Ca   | Ni    | Cu   | As   | Se   | Br  | Sr   | Cd   | I    |
|---------------------------|------|------|------|------|-------|------|------|------|-----|------|------|------|
| <i>A. victorii</i>        | 44.4 | 4.00 | 4.58 | 7.13 | 0.072 | 0.65 | 1.27 | 0.83 | 460 | 1.34 | 1.63 | 28.9 |
| <i>B. latissima</i>       | 53.4 | 5.62 | 5.08 | 11.4 | 0.74  | 0.99 | 4.68 | 1.25 | 550 | 1.83 | 1.19 | 73.5 |
| <i>B. parasitica</i>      | 57.2 | 4.36 | 1.74 | 9.06 | 0.49  | 1.52 | 3.25 | 1.79 | 330 | 1.47 | 1.83 | 58.3 |
| <i>P. maximus</i>         | 60.0 | 6.00 | 7.26 | 15.0 | 2.80  | 0.55 | 3.60 | 2.75 | 420 | 2.42 | 4.38 | 64.8 |
| <i>C. waggii pallidus</i> | 44.4 | 4.18 | 2.74 | 6.93 | 0.10  | 0.32 | 1.35 | 0.75 | 670 | 1.17 | 0.64 | 32.6 |
| <i>E. cruentus</i>        | 55.1 | 5.48 | 4.42 | 7.89 | 0.70  | 1.23 | 3.27 | 1.44 | 500 | 1.33 | 3.03 | 49.7 |
| <i>E. czerskii</i>        | 74.2 | 6.15 | 3.16 | 12.6 | 0.62  | 1.17 | 4.08 | 1.63 | 560 | 2.17 | 3.00 | 61.1 |
| <i>E. grandimanus</i>     | 67.4 | 5.64 | 2.09 | 9.50 | 0.72  | 1.93 | 3.97 | 2.10 | 590 | 1.55 | 1.34 | 74.7 |
| <i>E. lividus</i>         | 53.3 | 5.70 | 3.47 | 7.33 | 0.48  | 1.26 | 3.54 | 1.11 | 440 | 1.23 | 1.35 | 46.3 |
| <i>E. maackii</i>         | 43.8 | 6.06 | 2.28 | 6.93 | 1.05  | 0.79 | 3.82 | 1.25 | 590 | 1.15 | 0.66 | 39.7 |
| <i>E. verrucosus</i>      | 62.2 | 6.44 | 3.76 | 7.92 | 0.72  | 1.20 | 4.90 | 1.34 | 520 | 1.31 | 0.72 | 34.8 |
| <i>E. capreolus</i>       | 71.1 | 5.73 | 4.03 | 7.72 | 0.46  | 1.74 | 4.38 | 1.92 | 400 | 1.29 | 0.48 | 32.7 |
| <i>E. fuscus</i>          | 68.9 | 6.00 | 5.87 | 10.1 | 0.71  | 1.17 | 4.67 | 2.02 | 490 | 1.61 | 0.70 | 47.2 |
| <i>E. violaceus</i>       | 61.1 | 6.59 | 3.24 | 7.38 | 0.23  | 3.90 | 1.31 | 3.51 | 490 | 1.21 | 7.09 | 217  |
| <i>E. marituji</i>        | 55.6 | 5.36 | 2.37 | 6.63 | 0.82  | 1.43 | 3.72 | 1.29 | 380 | 1.16 | 0.67 | 22.7 |
| <i>E. viridis</i>         | 56.6 | 5.95 | 3.97 | 7.36 | 0.98  | 1.37 | 4.12 | 1.10 | 430 | 1.29 | 0.81 | 45.4 |
| <i>H. sophianosii</i>     | 73.3 | 5.45 | 4.16 | 9.50 | 0.20  | 1.26 | 2.73 | 2.25 | 530 | 1.68 | 0.83 | 42.6 |
| <i>P. cancellus</i>       | 45.0 | 4.79 | 4.55 | 8.02 | 0.44  | 0.68 | 4.09 | 1.06 | 400 | 1.53 | 0.34 | 37.9 |
| <i>P. kesslerii</i>       | 48.9 | 4.45 | 1.89 | 9.21 | 0.16  | 1.08 | 3.23 | 2.06 | 250 | 1.71 | 0.31 | 34.1 |

rii (Table 3). In the former species, the cuticle surface between complex microtriches, adsorbs many solid particles and shelter diatom algae (Fig. 6). According to Vinogradov's data [6], diatoms—epiphytes, often using amphipods as a substrate, concentrate Fe and Mn.

These features of the element composition of *E. violaceus* are largely related to their life pattern and diet. Crustaceans live on Baikal sponges, in which they carve out holes with the use of their strong mandibles [30, 45]. H. Morino and coauthors [45] consider this species a spongivore because of fragments of sponges with packed spicules found in their intestines. G.B. Gavrilov [8] found the intestines of all specimens he dissected to be empty. According to I.V. Mekhanikova's data, only two out of the 34 examined specimens had intestines filled with sponge fragments, 11 had few sponge fragments, and 21 specimens had their intestines empty [43]. The food for *E. violaceus* is most likely symbiotic algae, sponge cells, protozoa, fungi, and bacteria with high concentrations of Mn, Cu, Zn, Se, Mo, Cd, I [18, 47]. Large concentrations of Mn, Cu, Zn, Cd and small ratio Zn/Cu were also recorded in the element composition of Baikal gastropods *Megalovalvata baicalensis* [16], gathering their food from sponge surface [51]. The accumulation of Cu and Zn by coastal species of marine amphipods is mostly due to the element composition of the food, dominating in which are algae enriched with these elements [42].

The concentrations of Cu, Zn, As, Cd, Pb, and Hg in Baikal amphipods never exceeds the concentration of these elements in amphipods from relatively non-polluted or weakly polluted water bodies [23].

*P. maximus*, *E. grandimanus*, *P. kesslerii*, and *B. latissima* show higher concentrations of lithophilous elements (Al, Si, Sc, Ti, Ga, Y, Zr, Nb, Cs, Hf, Th, and REE) ( $p < 0.01$ ) against their very low concentrations in water (Table 3; Fig. 3). Among REE, dominating in amphipod composition are La and Ce, their highest concentration and largest REE amounts ( $p < 0.01$ ) were recorded in *Eulimnogammarus maackii*, *E. grandimanus*, *E. verrucosus*, *P. maximus*, *P. kesslerii*, *B. latissima* (Fig. 3). A potential source of lithophilous and other elements is fine mineral particles, consumed by amphipods with food. In the element composition of *B. latissima* with uncleaned alimentary canal, the concentrations of Al, Ti, Ga, Y, Zr, Nb, Cd, Pb, and REE are much higher than those in organisms kept without food (Fig. 4). Some chemical elements from consumed mineral particles can be transferred into solution by digestion and enter metabolic processes [39, 40]. Experiments show that the leaching of elements from mineral particles  $< 0.25$  mm in size is intensified by oxygen, carbon dioxide, organic acids, and other metabolic products of aquatic organisms [27]. The higher concentration of lithophilous elements can be due to the processes of sorption on the surface of chitinous exoskeleton [38].

The processes of bioaccumulation and mineralization form a single biological cycle of chemical elements. Bioaccumulation contributes to a decrease in the concentrations and reduces the migration of chemical elements in the environment. Conversely, the mineralization of organic residues increases the migration capacity of elements and enriches surface water with them [25].

The wide spectrum of chemical elements, accumulated in amphipod exoskeleton (Fig. 5), periodically returns into biogeocenoses of the shallow zone as the result of moulting. Some exuviae are ate by aquatic organisms, while some others accumulate in coastal detritus deposits, which are actively consumed by organisms of the splash zone [32]. Compounds of Na, Cl, and K are most rapidly washed out from the tissues of dead amphipods, which also are a common component of coastal accumulations (Fig. 2).

The examined amphipods show little variations in their ability to accumulate S, Cl, alkaline-earth (Ca, Mg, Sr, Ba) and alkaline (Na, K, Rb) elements. At higher Na concentration in littoral zone water (Na/K of 3.2–3.5), Baikal amphipods, as well as marine crustaceans [6, 36] concentrate more K (Table 4).

The examined amphipods accumulate P, Br, and Zn in nearly the same amounts. The difference between Cu and Cd concentration by different species is more pronounced. The maximal BACs of Cu and Cd, which are ~2 times higher than the BACs of other amphipods, are typical of *E. violaceus*. This species also shows higher degree of I accumulation. The specimens of other species accumulate 3–8 times lesser amounts of this element (Table 4). *E. violaceus* is among the most active concentrators of Mn (BAC ~3500) and Se (BAC ~1750). Many among the examined amphipods show  $BAC_{Mn}$  and  $BAC_{Se}$  of 400–1000. The above elements accumulate in large amounts in benthic macroalgae of the littoral zone [17, 19], which form an important food component of the majority of the examined amphipod species (Table 1). Among all elements, those concentrated by amphipods to the least extent relative to water are B (BAC < 10), Li and Bi (10–50), as well as Mo, Mg, U, Si, W, Sc, Fe, V, and Sn (BAC ~ 10–100).

By the value of  $BAC > 2$  relative to the stone substrate [23], the examined amphipods are macroconcentrators of Br, P, I, Ca, S, Cl, and (except for *A. victorii*, *C. waggii pallidus*, and *E. violaceus*), As. In addition to these elements, many amphipod species accumulate Se. Deconcentrators of Se (BAC < 1) are *A. victorii* and *C. waggii pallidus*. The  $BAC_{Cu}$  was maximal for *E. violaceus*. In the composition of organisms of other species, the concentration of Cu is the same or slightly greater than that in BS. Many amphipod species are microconcentrators (BAC of 1–2) or deconcentrators (BAC < 1) of Cd. To the greatest extent, this element is accumulated by *E. violaceus*, *P. maximus*, *E. cruentus*, *E. czerskii*. In their composition, Cd con-

centration is 3–7 times that in the stone substrate (Table 5). Cu and Cd is often concentrated relative to coarse-detritus silt by amphipods of non-polluted and weakly polluted freshwater ecosystems ( $BAC_{Cu}$  is 1.0–1.8, and  $BAC_{Cd}$  is 0.6–1.5) [23]. Relative to the stone substrate, the BAC of other elements in the examined amphipods is  $\ll 1$  and, as a rule, the BAC decreases with the atomic number of the element.

## CONCLUSIONS

The dominating macroelements in the composition of the examined amphipod species are  $Ca > P \geq S > K \geq Na > Cl > Mg$ ; the dominating microelements are Sr, Br, Si, Ba, Fe, Zn, Al, Cu, Mn. The minimal concentrations were recorded for Be, Nb, Pd, Sb, Cs, Eu, Tb, Tm, Lu, Au, Hf, Ta, and Bi. In 2003–2006, the concentrations in Baikal amphipods of Cu, Zn, As, Cd, Pb, and Hg, which are toxic in higher concentrations, never exceeded the concentrations of these elements in amphipods from relatively non-polluted aquatic ecosystems.

No pronounced differences were found in the element composition of the majority of the examined amphipods with similar food spectra, living within the same depth range on the same soil types.

Among all examined species, a symbiont of Baikal sponges *E. violaceus* can be isolated by its microelement composition. The highest concentration of Cu, I, and Cd in its composition and the minimal values of Cu/Zn and Fe/Mn are due to its mode of life and the specifics of nutrition.

The concentrations of the analyzed elements in the amphipods of Baikal littoral zone is far in excess of their concentration in water. The degrees of concentration in amphipods relative to water are largest for  $P > Br > Cu > Zn > Cd$ , and those relative to stone substrate are largest for  $Br > P \geq I > Ca > S > Cl \geq As > Sr$ , many species also accumulate Se, Cu, and Cd.

The obtained data on the macro- and microelement composition of amphipods can be used as background values in the environmental monitoring of Baikal littoral zone with super-low concentrations of many chemical elements in water. Among the examined species, the most promising are symbionts of Baikal sponges (*B. parasitica*, *E. violaceus*) and *B. latissima* and *E. viridis*, *E. verrucosus*, widespread on the stony littoral of Baikal. These species are of relatively small size, can be collected in a sufficient amount, and are closely related with the substrate; algae and detritus are important food components of *B. parasitica*, *B. latissima*, *E. viridis*, and *E. verrucosus*. In the tissues of giant species, which can move over considerable distances and avoid polluted coastal areas, the accumulation of the elements under consideration can remain at the background level.

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